Theoretical Study on the Bridging Ability of Oxygen and Sulphur in Vinyl Cations

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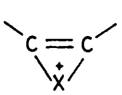
A non-empirical SCF-MO investigation with split-valence basis sets was performed on $C_2H_2OH^+$ and $C_2H_2SH^+$ cations. The four limiting structures corresponding to pyramidal and planar bridged ions and to s-*cis*- and s-*trans*-vinyl cations were fully optimized and interconnected through an energy surface. In both cases the planar bridged structure is on an energy maximum, whereas the other three structures correspond to stable conformations. The geometrical and electronic properties of the limiting structures are discussed as well as the interconversion processes among them.

THE relative stabilities of bridged ions (1) with respect to open ions (2), formally regarded as addition of X^+ to an acetylene derivative, are attracting considerable interest because they may play quite a significant role in either electrophilic addition to acetylenes or in solvolysis of β-X-vinyl derivatives.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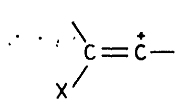
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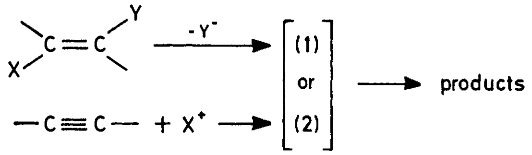

Different relative stabilities are theoretically expected, and in some cases experimentally found, with changes of X. A particular case of theoretical and practical interest is that of the pair X = SR and X = OR. Indeed a large body of evidence indicates that bridged ions (1) play a major role in both the addition of sulphenyl halides to acetylenes and the solvolysis of β-thiovinyl sulphonates.[1] This experimental evidence was recently substantiated by the detection [2] by n.m.r. spectroscopy of a few examples of thiirenium ions (1; X = SR) and by a theoretical study of the isomeric $C_2H_2SH^+$ ions which showed that the two valence tautomers have similar energies [3] (ΔE_{2-1} *ca.* 4 kcal mol^{-1}).

On the contrary the reactivity of β-oxyvinyl derivatives indicates very poor, if any, ability by oxygen to give bridged structures,[4] although data on the oxidation of some acetylene derivatives with peroxyacids suggests the possibility of an oxirenium-type structure (1; X = OR) as transition state or intermediate.[5]

With the aim of gaining a better insight into this problem and continuing our theoretical studies on cations of the general structure $C_2H_2X^+$ (X = SH,[3] F,[6] and Cl [7]), we report our results on the computed relative stabilities of (1) and (2) for X = OH and a comparison of them with those for X = SH. Although we had already computed the relative energies of (1) and (2) for X = SH by an *ab initio* SCF-MO method,[3] data for these species have been recomputed using a basis set comparable with that used for the oxygen analogue to make the comparison significant. More extensive geometry optimizations were also performed. Consequently the results for the $C_2H_2SH^+$ ions are somewhat different from those previously reported.[3]

METHOD

Single determinant molecular wave functions were constructed from molecular orbitals, which in turn were generated from Gaussian type functions by a LCAO-SCF-MO method. A split-valence basis set was used: in particular a 6-31G basis set was used for the $C_2H_2OH^+$ system and a 4-31G basis set for the $C_2H_2SH^+$ system. Computations were performed on a CDC CY76 computer at the Computing Laboratory in Bologna using the Gaussian 70 program system.[8]

The geometry optimizations were carried out with the procedure already used in our earlier investigations on $C_2H_2X^+$ species,[3,6,7] namely only one geometrical parameter was varied at a time while the remaining parameters were kept constant.

RESULTS

The geometry optimizations were carried out on four oxygen-containing species (3)—(6) (Z = O) and on four sulphur-containing species (3)—(6) (Z = S), corresponding to the pyramidal (3) and planar (4) cyclic cations and to the s-*cis*- (5) and s-*trans*-vinyl cations (6). Tables 1 and 2 summarize the optimized geometries and relative energies as well as the energy components for the $C_2H_2OH^+$ species and for the $C_2H_2SH^+$ species respectively.

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[1] G. Modena and G. Scorrano, *Reaction Mechanism Sulfur Compounds*, 1968, **3**, 115; G. Modena and U. Tonellato, *Adv. Phys. Org. Chem.*, 1971, **9**, 185; P. S. Stang, *Progr. Phys. Org. Chem.*, 1973, **10**, 276; G. Modena, G. Scorrano, and U. Tonellato, *J.C.S. Perkin II*, 1973, 493.

[2] G. Capozzi, O. DeLucchi, V. Lucchini, and G. Modena, *J.C.S. Chem. Comm.*, 1975, 248.

[3] I. G. Csizmadia, A. J. Duke, V. Lucchini, and G. Modena, *J.C.S. Perkin II*, 1974, 1808.

[4] G. Capozzi and G. Modena, *J.C.S. Perkin I*, 1972, 216; U. Tonellato and G. Versini, *Gazzetta*, 1975, **105**, 1237.

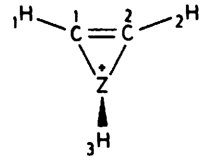
[5] K. M. Ibne-Rasa, R. H. Peter, J. Ciabattoni, and J. O. Edwards, *J. Amer. Chem. Soc.*, 1973, **95**, 7894.

[6] I. G. Csizmadia, V. Lucchini, and G. Modena, *Theor. Chim. Acta*, 1975, **39**, 51.

[7] V. Lucchini, G. Modena, and I. G. Csizmadia, *Gazzetta*, 1975, **105**, 675.

[8] W. J. Hehre, W. A. Lathan, R. Dichfield, M. D. Newton, and J. A. Pople, Gaussian 70, Quantum Chemistry Program Exchange no. 236, Indiana University, Bloomington, Indiana.

The cyclic structures (3) and (4) have been optimized with the symmetry constraints characteristic to them.



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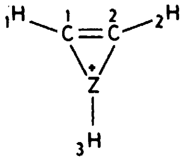

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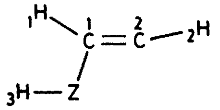

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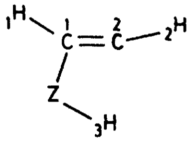

(6)

Pyramidal thiirenium ion (3; Z = S), more stable than both β-thiovinyl cations (5) and (6) (Z = S), corresponds to a true minimum of the energy hypersurface, whereas pyramidal oxirenium ion (3; Z = O), energetically less favoured than both β-oxyvinyl cations (5) and (6) (Z = O), may not correspond to a minimum if a second partial derivative with respect to any geometrical parameter is negative. Because of this possibility the pyramidal oxirenium ion was reoptimized neglecting any symmetry constraint. The reoptimization leaves the geometrical parameters virtually unchanged, while energy is lowered only 0.17 kcal mol^{-1}. This change is too small for reversing the previously observed relative energy trend (ΔE −21.82 kcal mol^{-1}).

The four valence tautomers (3)—(6) have been connected through an energy surface (Figure 1 for Z = O and Figure 2 for Z = S), with the aid of several other computed points (*ca.* 20) corresponding to geometries intermediate among the above four limiting structures. The upper horizontal border of both surfaces describes the *cis–trans*-isomerization of β-Z-vinyl cations, while the lower horizontal border describes the pyramidal inversion process of cyclic structures. The vertical borders link planar structures through an in-plane movement of all atoms. In order to connect the two processes described along the horizontal borders, a pivot direction is chosen, which is the Z–C(1) bond in open structures and the bisector of the $C(1)\widehat{Z}C(2)$ angle in closed ones. In intermediate structures the pivot direction varies between these two extremes. The angle between the

TABLE 1

Optimized geometries [a] and corresponding energies [b] as computed with 6-31G basis set for $C_2H_2OH^+$ species

	Pyramidal oxirenium ion (3)	Planar oxirenium ion (4)	s-*cis* β-Oxyvinyl cation (5)	s-*trans*- β-Oxyvinyl cation (6)
$r[C(1)-C(2)]$	1.263 04	1.280 86	1.294 01	1.294 36
$r[C(1)-O]$	1.586 04	1.534 08	1.339 06	1.356 28
$r[C(1)-H(1)]$	1.073 92	1.073 68	1.090 90	1.093 57
$r[C(2)-H(2)]$	1.073 92	1.073 68	1.078 31	1.079 44
$r[O-H(3)]$	0.974 30	0.971 19	0.966 28	0.970 84
$O\widehat{C}(1)C(2)$	66.53	65.33	123.00	132.24
$H(1)\widehat{C}(1)C(2)$	166.68	164.48	115.08	113.14
$C(1)\widehat{C}(2)H(2)$	166.68	164.48	175.49	175.16
$H(3)\widehat{O}C(1)$	117.08	155.33	117.50	117.43
α [c]	119.76	180.00		
$E_{nuclear}$	67.051 156	67.636 302	64.216 201	63.615 387
$E_{electronic}$	−218.880 492	−219.438 430	−216.080 308	−215.473 817
Total energy	−151.829 336	−151.802 128	−151.864 107	−151.858 430
Relative energy [d]	0.00	17.07	−21.82	−18.25

[a] Bond lengths in Å, angles in degrees. [b] hartree. [c] See text. [d] kcal mol^{-1}.

TABLE 2

Optimized geometries [a] and corresponding energies [b] as computed with 4-31G basis set for $C_2H_2SH^+$ species

	Pyramidal thiirenium ion (3)	Planar thiirenium ion (4)	s-*cis*- β-Thiovinyl cation (5)	s-*trans*- β-Thiovinyl cation (6)
$r[C(1)-C(2)]$	1.254 42	1.289 71	1.265 29	1.267 77
$r[C(1)-S]$	2.051 48	1.912 41	1.818 13	1.822 72
$r[C(1)-H(1)]$	1.071 37	1.066 56	1.086 78	1.086 01
$r[C(2)-H(2)]$	1.071 37	1.066 56	1.068 60	1.068 88
$r[S-H(3)]$	1.368 18	1.355 78	1.355 49	1.358 54
$S\widehat{C}(1)C(2)$	72.20	70.30	126.54	131.93
$H(1)\widehat{C}(1)C(2)$	161.54	154.61	115.42	116.75
$C(1)\widehat{C}(2)H(2)$	161.54	154.61	178.50	179.45
$H(3)\widehat{S}C(1)$	97.58	160.30	94.94	98.33
α [c]	97.96	180.00		
$E_{nuclear}$	88.511 702	91.369 451	84.835 094	84.488 013
$E_{electronic}$	−562.541 490	−565.281 257	−558.860 568	−558.513 173
Total energy	−474.029 788	−473.911 806	−474.025 474	−474.025 160
Relative energy [d]	0.00	74.03	2.71	2.90

[a] Bond lengths in Å, angles in degrees. [b] hartree. [c] See text. [d] kcal mol^{-1}.

H(3)–Z bond and the pivot direction varies from the H(3)$\hat{Z}$C(1) angle value in open structures to the angle α * in closed ones, and the H(3) atom is rotated around the pivot axes as to ensure a monotonic variation of its height above the plane of the molecule. A curve fitting method using splines under tension [9] was used to fit the computed points and to generate the energy of the molecule at the intermediate positions. The dotted lines in Figures 1 and 2 correspond to the lowest energy paths connecting the open structures with the pyramidal bridged ions.

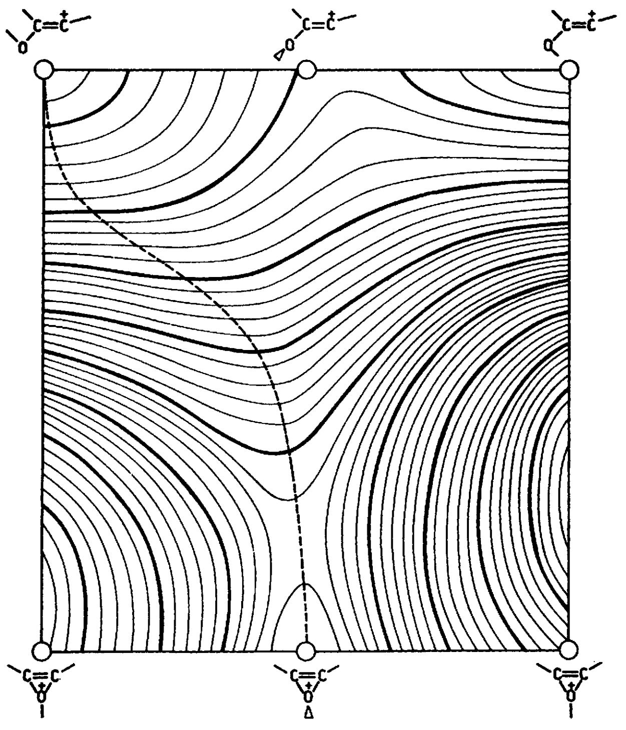

FIGURE 1 Energy surface for the $C_2H_2OH^+$ system. The energy difference between isoenergetic lines is 1 (thin lines) and 5 kcal mol^{-1} (thick lines)

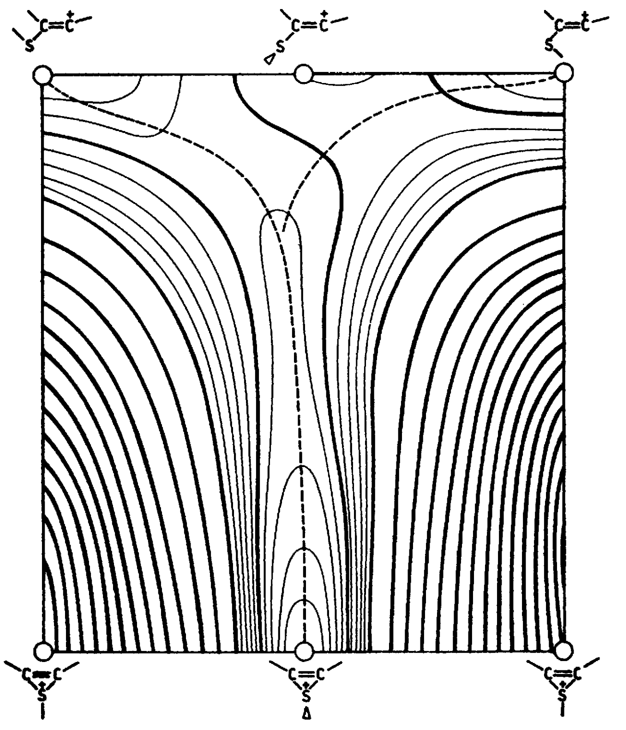

FIGURE 2 Energy surface for the $C_2H_2SH^+$ system. The energy difference between isoenergetic lines is 1 (thin lines) and 5 kcal mol^{-1} (thick lines)

The energy profiles for the interconversion from the more stable s-*cis*-open structures are reported in Figure 3 (dotted lines). For the sake of comparison we also give the energy profiles (solid lines) calculated with the same procedure adopted in our earlier investigations,[3,6,7] that is with the assumption that the motions of all the atoms are occurring in a synchronized fashion.

In order to test in the cyclic structures the dependence of the total energy and of the out-of-plane angle α from the variation of the bond angles around the heteroatoms [see Discussion section, part (ii)], we have investigated in detail the model systems H_3O^+ and H_3S^+, using again the same basis sets adopted for the $C_2H_2OH^+$ and $C_2H_2SH^+$ systems respectively.

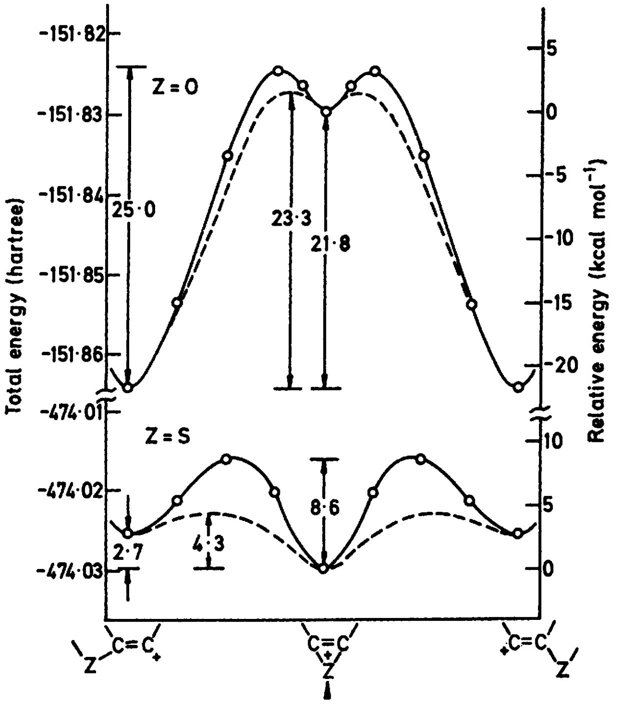

FIGURE 3 Energy profiles for the interconversion between the s-*cis*-vinyl cations and the pyramidal bridged ions (for details, see text)

The oxonium and sulphonium models were computed in the pyramidal and planar conformations. The pyramidal (or planar) conformation was first optimized neglecting any geometrical constraint, then we imposed on one of the HZH angles the values found for the corresponding C(1)ZC(2) angle in the pyramidal (or planar) Z-irenium ion, while all remaining geometrical parameters were allowed to relax to the optimum value. The results of these computations are collected in Tables 3 and 4.

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* We define α as the angle between the H(3)–Z bond and the bisector of the C(1)$\hat{Z}$C(2) angle (α is 180° for planar structures).

[9] A. K. Cline, *Communications of the Association for Computing Machinery*, 1974, **17**, 218.

It may be noticed that the optimum unconstrained conformation of the H_3O^+ ion corresponds to a planar structure.

TABLE 3

Geometries [a] and corresponding energies [b] as computed with 6-31G basis set for H_3O^+ species

	Constrained		
	Pyramidal H_3O^+	Planar H_3O^+	Unconstrained Planar H_3O^+
r[H(1)–O] = r[H(2)–O]	1.079 45	1.030 99	0.965 41
r[H(3)–O]	0.990 62	0.986 59	
$H(1)\widehat{O}H(2)$	46.94 [c]	49.35 [d]	120.00
α [e]	114.36	180.00	
$E_{nuclear}$	13.347 979	13.654 786	14.104 474
$E_{electronic}$	−89.461 114	−89.743 313	−90.380 788
Total energy	−76.113 135	−76.088 527	−76.276 315
Relative energy [f]	0.00	15.44	

[a] Bond lengths in Å, angles in degrees. [b] hartree. [c] $C(1)\widehat{O}C(2)$ in pyramidal oxirenium ion. [d] $C(1)\widehat{O}C(2)$ in planar oxirenium ion. [e] See text. [f] kcal mol^{-1}.

Kollman and Bender [10] have found, using a more extended basis set, a slight pyramidal structure. However the deviation from planarity and the pyramidal inversion barrier are so small, when compared with the corresponding parameters in oxirenium ion and in the constrained H_3O^+ model, that this discrepancy is irrelevant for the purposes of our discussion.

TABLE 4

Geometries [a] and corresponding energies [b] as computed with 4-31G basis set for H_3S^+ species

	Constrained		Unconstrained	
	Pyramidal H_3S^+	Planar H_3S^+	Pyramidal H_3S^+	Planar H_3S^+
r[H(1)–S] = r[H(2)–S]	1.520 44	1.422 17	1.363 74	1.338 09
r[H(3)–S]	1.372 67	1.387 42		
$H(1)\widehat{S}H(2)$	35.60 [c]	39.40 [d]	99.99	120.00
α [e]	93.31	180.00		
$E_{nuclear}$	18.377 506	18.943 393	19.385 193	19.667 312
$E_{electronic}$	−416.739 556	−417.174 556	−417.845 003	−418.097 967
Total energy	−398.362 051	−398.231 163	−398.459 810	−398.430 653
Relative energy [f]	0.00	82.13	0.00	18.29

[a] Bond lengths in Å, angles in degrees. [b] hartree. [c] $C(1)\widehat{S}C(2)$ in pyramidal thiirenium ion. [d] $C(1)\widehat{S}C(2)$ in planar thiirenium ion. [e] See text. [f] kcal mol^{-1}.

DISCUSSION

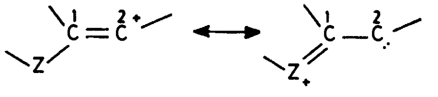
The results of our computations, which are summarized as energy surfaces in Figures 1 and 2, present several interesting features which deserve comments. They will be dealt with in terms of the principal interconversion processes among the four fundamental structures.

(i) cis–trans-*Isomerisation of* β-Z-*Vinyl Cations*.—The full geometry optimization of the β-oxyvinyl cation revealed that there are two energy minima corresponding to the s-*cis*- (5) and to the s-*trans*-conformations (6). The s-*cis*-conformer is more stable with an energy separation of 3.57 kcal mol^{-1}. The barrier to rotation was found to be 7.17 kcal mol^{-1}, considerably higher than that measured for the rotation around the C–O bond in methanol (1.07 kcal mol^{-1}).[11]

The β-thiovinyl cation presents the same general features. However in this case the two conformers have practically the same energy (the energy separation is 0.19 kcal mol^{-1}). The barrier to rotation from the slightly more stable s-*cis*-form to the s-*trans*-form is smaller (3.31 kcal mol^{-1}) than that of the oxygen analogue, but also in this case the barrier is somewhat higher than that found in methanethiol (1.27 kcal mol^{-1}).[12]

Other features of interest are the C(1)–C(2) bond lengths, which are longer in the β-oxyvinyl cations than in the β-thiovinyl cations, the deviation from collinearity of the $C(1)\widehat{C}(2)H(2)$ bond angles, which is more marked for the β-oxyvinyl cations, and the C(1)–O and C(1)–S bond lengths, which are shorter than those measured or computed in methanol (measured [11] 1.425, computed [13] 1.439 Å) and in methanethiol (measured [12] 1.819, computed [14] 1.881 Å).*

The high rotational barriers and the above geometrical features may suggest that in these cations the C(1)–Z bond should have a certain degree of π character and that the corresponding conjugative stabilization is greater in the case of β-oxyvinyl cations than in that of β-thiovinyl cations. The latter statement is also in agreement with the amounts of π charge transfer, which are 0.138 7 and 0.102 0 in the s-*cis*-β-oxyvinyl cation and in the *s-cis*-β-thiovinyl cation respectively.†



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* The shortening of the C(1)–S bond in β-thiovinyl cations appears to be small but significant when the comparison is made with the computed C–S bond length in methanethiol, but it vanishes when compared with the experimental bond length. However the quoted data indicate that the basis set used overestimates the C–S bond length in methanethiol and possibly also in β-thiovinyl cations.

† If we denote the gross orbital charge of the heteroatom lone pair with Q_X, then $2 - Q_X$ represents the amount of π charge transfer. If such value is positive the charge transfer occurs from the heteroatom lone pair to the olefin π system. The values for Q_O and Q_S are (in the s-*cis*-isomers) 1.861 3 and 1.898 0 respectively. This latter value was obtained assuming a nominal gross orbital charge for the $2p\pi$ sulphur orbital of (2); the actual values are 1.977 3 and 1.920 7 for sulphur $2p\pi$ and $3p\pi$ orbitals respectively.

[10] P. A. Kollman and C. F. Bender, *Chem. Phys. Letters*, 1973, **21**, 271.

[11] R. M. Lees and J. G. Baker, *J. Chem. Phys.*, 1968, **12**, 5299.

[12] T. Kojima, *J. Phys. Soc. Japan*, 1960, **15**, 1284.

[13] W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Progr. Phys. Org. Chem.*, 1974, **11**, 236.

[14] J. B. Collins, P. R. Schleyer, J. S. Binkly, and J. A. Pople, *J. Chem. Phys.*, 1976, **64**, 5142.

(ii) *Pyramidal Inversion of the Cyclic Ions.*—The most stable cyclic structure, both for the oxy- and the thio-compounds, corresponds to a pyramidal arrangement around the heteroatom. The optimized bridged structures have an out-of-plane angle α of 120° for oxirenium ion and 98° for thiirenium ion.

The planar bridged structures, characterized by considerably higher energy, may be considered as the transition states for the formal process of pyramidal inversion. This process is accompanied by a lengthening of the C(1)–C(2) bond and a shrinkage of the bonds associated with the inverting atom. This bond shortening phenomenon is more pronounced in the case of C–Z bonds than in the case of Z–H(3) bond, and much larger for thiirenium ion than for oxirenium ion. This is in agreement with earlier observations, since bond shortening in pyramidal inversion is a well known phenomenon.[15]

The energetics of pyramidal inversion is also noteworthy. It is very large in the case of thiirenium ion (74.03 kcal mol^{-1}) and much smaller in the case of oxirenium ion (17.07 kcal mol^{-1}). Both values are considerably higher than the barriers to inversion for oxonium and sulphonium ions.[16] *A priori* the factors which might be responsible for these facts are either π or σ interactions or both.

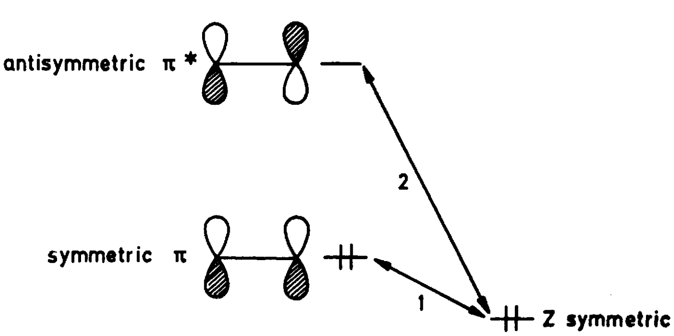

FIGURE 4 Interaction diagram between the π MOs of the olefinic fragment and the heteroatom lone pair. The MOs are symmetric or antisymmetric with respect to the σ_v plane of the composite system

The role played by π effects are better understood discussing first the planar structures. In the planar structures the π system may adequately be represented by considering the interactions occurring between the heteroatom lone pair and the π orbitals of the olefin double bond. The related interaction diagram is shown in Figure 4. Both in planar oxirenium ion and in planar thiirenium ion the only symmetry allowed interaction is the four electron–two orbital interaction (1) which is destabilizing. It is evident that this destabilizing character is reduced through pyramidalization because doing so the overlap between the two interacting orbitals is reduced. In conclusion the π interactions dictate a pyramidal structure.

The effects of the σ interactions are well demonstrated by the computations carried out on the H_3O^+ and H_3S^+ ions, since in these models the π interactions are not present. Inspection of Tables 3 and 4 reveals that the shrinking of one of the $H\hat{Z}H$ angles to the values of the cyclic structures is sufficient to reproduce satisfactorily the out-of-plane angle α of the pyramidal cyclic ions and the energies of the pyramidal inversion process. Other facts associated with the pyramidal inversion, such as the shortening of the bond lengths around the heteroatom and the variation in nuclear repulsion and total electronic energies, are qualitatively reproduced by the models adopted.

In conclusion we may assume with confidence that the dominant factors in the inversion process of oxirenium and thiirenium ions are basically the same σ factors operating in the inversion process of the model H_3Z^+ ions, but modified somewhat by the ring strain. The π effects act in the same direction even if their contribution is considerably less. The present results confirm the conclusions anticipated in the previous work[3] on $C_2H_2SH^+$.

(iii) *Interconversion between Open and Bridged Structures.*—Now turning to the point of greatest chemical interest, namely the relative stabilities of open and bridged structures, we notice that both systems present three local minima corresponding to the two s-*cis*- and s-*trans*-β-Z-vinyl cations and to the pyramidal Z-irenium ion. However in the case of the oxy-compounds the oxirenium ion is 21.82 kcal mol^{-1} above the most stable s-*cis*-β-oxyvinyl cation, whereas in the case of the thio-compounds the open and bridged structures have very similar energies, with the thiirenium ion being more stable than the s-*cis*-β-thiovinyl cation by 2.90 kcal mol^{-1} only.

The interconversion process in going from open to bridged structures can be conveniently described in terms of two independent motions: (i) out-of-plane motion of H(3) [rotation about the Z–C(1) bond] and (ii) ring closure [contraction of the $Z\hat{C}(1)C(2)$ angle].

For the conversion of the s-*cis*-β-oxyvinyl cation into the oxirenium ion, inspection of Figure 1 reveals that the two motions [(i) and (ii)] are not synchronous (dotted line): ring closure is dominant at the beginning and at the end of the process, whereas the out-of-plane movement of H(3) is significant only in the central part of the conversion. The point of maximum energy (Figure 3) occurs very near to the bridged structure and is only 1.50 kcal mol^{-1} above it. On the other hand the direct conversion of the s-*trans*-β-oxyvinyl cation into oxirenium ion seems to be unrealistic, since the lowest energy path is characterized by full rotation around the C(1)–O bond, that is isomerisation to the s-*cis* conformer, followed by conversion of the latter to the cyclic ion.

In the sulphur case the two paths are almost symmetric (Figure 2), being characterized by an early out-of-plane motion of H(3). The point of maximum energy (Figure 3) is only a few kcal above the two

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[15] E. Kari and I. G. Csizmadia, *J. Chem. Phys.*, 1969, **50**, 1443.

[16] A. Rauk, J. D. Andose, W. G. Frick, R. Tang, and K. Mislow, *J. Amer. Chem. Soc.*, 1971, **93**, 6507.

minima, suggesting a very easy conversion from the bridged to either one of the open structures.

Conclusions.—The general features of the surface for the thio-system (Figure 2) show that there are very easy paths for the interconversion of the two enantiomeric pyramidal thiirenium ions *via* either the s-*cis*- or the *s-trans*-β-thiovinyl open structures, whereas the pure pyramidal inversions seem energetically forbidden. Furthermore it appears that the *cis–trans*-isomerisation process may occur with almost equal ease *via* the bridged structure and not only through rotation.

The oxy-system (Figure 1) presents significantly different features. The process of pyramidal inversion of oxirenium ion is not in this case formally forbidden, as the barrier is only 17.07 kcal mol^{-1}. However the very small energy barrier (1.50 kcal mol^{-1}) towards the conversion to the much more stable s-*cis*- or s-*trans*-open structures makes an inversion process not realistic. As far as the *cis–trans*-isomerisation process of the open structures is concerned, the only viable path seems to be the rotation about the C(1)–O bond.

We are aware that the relative stabilities of the various valence tautomer and the energetics of the interconversion paths may be modified by extending the calculations beyond the HF limits as well as, if not more so, by substituting the hydrogen atoms with more appropriate groups. However we feel that these factors should not drastically change the general features emerging from our analysis. Indeed they are in quite a a good agreement with and offer a satisfactory rationale to the available experimental results.

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